

Supporting Information for:

Intermetallic transfer of unsymmetrical borylene fragments: isolation of the second early-transition-metal terminal borylene complex and other rare species

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Synthetic and Spectroscopic Details

General considerations. All manipulations were performed either under an atmosphere of dry argon or *in vacuo* using standard Schlenk line or glovebox techniques. Pentane and hexane were dried and degassed by refluxing over Na/K amalgam under an atmosphere of dry argon. Diethyl ether (Et₂O) and tetrahydrofuran (THF) were dried and degassed by refluxing over Na/benzophenone complex and K/benzophenone complex (ketyl), respectively, under an atmosphere of dry argon. Toluene and benzene were dried and degassed by refluxing over molten sodium and potassium, respectively, under an atmosphere of dry argon. Hexamethyldisiloxane (C₆H₁₈OSi₂) was dried over molecular sieves (4 Å) and degassed by three freeze-pump-thaw cycles before use. [(OC)₅Cr(NMe₃)], [(OC)₅W(NMe₃)], [(OC)₅Mo(NMe₃)], Na₂[Mo(CO)₅], Na₂[Cr(CO)₅], Na₂[W(CO)₅],¹ [(η⁵-C₅H₅)V(CO)₄], [(η⁵-C₅H₅)₂Ni₂(CO)₂],² [(η⁵-C₅H₄Me)Co(CO)₂],³ [(η⁵-C₅Me₅)Ir(CO)₂],⁴ HN(SiMe₃)(*t*Bu)⁵ were synthesised by standard literature procedures. Deuterated benzene (C₆D₆) was dried and degassed by refluxing over LiAlH₄ under an atmosphere of dry argon. All dried solvents (both deuterated and non-deuterated) were stored under argon over activated molecular sieves. Photolytic experiments were performed in quartz Schlenk flasks or J. Young tubes. The light source was a LOT-Oriel photolysis apparatus with a 500 W Hg/Xe arc lamp equipped with infrared filters, irradiating at 210-600 nm. NMR spectra of isolated compounds were either acquired on a Bruker Avance 500 NMR spectrometer or a Bruker Avance 400 NMR spectrometer. Chemical shifts (δ) are given in ppm. ¹H and ¹³C{¹H} NMR spectra were referenced to external SiMe₄ by residual protic solvent (¹H) or the solvent itself (¹³C). ¹¹B{¹H} and ¹⁰B{¹H} NMR spectra were referenced to external BF₃.OEt₂. ²⁹Si{¹H} NMR spectra were referenced to external SiMe₄. IR data were acquired on a JASCO FT/IR-6200typeA apparatus. UV-vis spectra were acquired on a JASCO-V660 UV-vis spectrometer. Differential thermoanalysis (DTA) were performed on an Elementar Vario MICRO cube elemental analyser.

Synthesis of Br₂BN(SiMe₃)(*t*Bu). A solution of HN(SiMe₃)(*t*Bu) (20.0 g, 138 mmol) in hexane (50 mL) was treated with *n*BuLi (1.6 M in hexane, 86 mL, 140 mmol) at 0 °C for a period of 3 h. After the 3 h period, the reaction was allowed to warm to room temperature and stir for a period of 21 h. BBr₃ (13.1 mL, 34.6 g, 138 mmol) was then added dropwise to the reaction mixture over the course of 3 h with stirring for an additional period of 24 h at room temperature. Workup of this reaction mixture was undertaken by filtration of the solids and removal of all volatiles from the filtrate under high vacuum (0.001 Torr). The residual oil was distilled under high vacuum (0.001 Torr) at 43 °C to yield Br₂BN(SiMe₃)(*t*Bu) (27.8 g, 88.3 mmol) as a clear colorless oil in 64% yield. ¹H NMR (500.13 MHz, CDCl₃, 297 K) [ppm]: δ = 1.49 (s, 9H, C-(CH₃)₃), 0.41 (s, 9H, Si-(CH₃)₃), ²J_{H-Si} = 6.6 Hz). ¹³C{¹H} NMR

(125.77 MHz, CDCl₃, 297 K) [ppm]: δ = 57.6 (s, 1C, C-(CH₃)₃), 32.7 (s, 3C, C-(CH₃)₃), 5.8 (s, 3C, Si-(CH₃)₃, ¹J_{C-Si} = 58 Hz). ¹¹B{¹H} NMR (160.47 MHz, CDCl₃, BF₃.OEt₂, 297 K) [ppm]: δ = 36.4 (s). ²⁹Si{¹H} NMR (79.49 MHz, CDCl₃, SiMe₄, 297 K) [ppm]: δ = 7.8 (s).

Synthesis of [(OC)₅Cr{BN(SiMe₃)(tBu)}] (1a). A solution of [(OC)₅Cr(NMe₃)] (1.03 g, 4.10 mmol) in THF (5 mL) was cooled to -78 °C and a solution of Na[C₁₀H₈] (41 mL, 0.20 M in THF) was added dropwise over a period of 10 min. After the addition was completed, all volatile materials were removed under high vacuum (0 °C/0.001 Torr) and the remaining brown/yellow solids were dissolved with Et₂O (20 mL) and triturated in an ultrasonic bath for 2 min to extract the remaining naphthalene from the crude material. The reaction mixture was separated by centrifugation to concentrate Na₂[Cr(CO)₅] as a yellow solid with a Et₂O supernatant. The supernatant was subsequently decanted and the process repeated two additional times (2 x 20 mL Et₂O) in order to remove residual naphthalene. The remaining solid precipitate was dried briefly to yield Na₂[Cr(CO)₅] as a light brown/yellow powder. This powder was then suspended in toluene and cooled to -78 °C, after which Br₂BN(SiMe₃)(tBu) (1.3 g, 4.1 mmol) was added dropwise by syringe. The reaction mixture was then stirred at -78 °C for one hour after which the color of the reaction mixture changed from light yellow to dark brown. The reaction flask was removed from the cold bath and allowed to stir for an additional hour while slowly warming to room temperature. Over the course of this additional hour the reaction changed to a completely opaque black suspension. All volatiles were then removed under high vacuum (0.001 Torr) and the black solid was dissolved in pentane (20 mL). This pentane suspension was triturated in an ultrasonic bath for a period of 2 min and separated by centrifugation to concentrate the salt elimination byproduct from a black pentane supernatant. Filtration of the supernatant yielded a black pentane filtrate, which precipitated colorless crystalline solids upon storage at -78 °C after a period of 24 h. These colorless crystalline solids correspond to a crude sample of [(OC)₅Cr{BN(SiMe₃)(tBu)}], which could be further purified by redissolving the crude material in pentane and storage in a -78 °C freezer for an additional period of 24 h. Removal of the supernatant from the subsequent crystalline material and drying of the product under high vacuum yielded analytically pure [(OC)₅Cr{BN(SiMe₃)(tBu)}] (0.555 g, 1.60 mmol) in 39% yield. Crystals suitable for X-ray diffraction were grown from saturated solutions of [(OC)₅Cr{BN(SiMe₃)(tBu)}] in hexane. ¹H NMR (500.13 MHz, C₆D₆, 297 K) [ppm]: δ = 1.15 (s, 9H, C-(CH₃)₃), 0.16 (s, 9H, Si-(CH₃)₃, ¹J_{H-Si} = 6.7 Hz). ¹³C{¹H} NMR (125.77 MHz, C₆D₆, 297 K) [ppm]: δ = 218.4 (s, 1C, *trans*-CO to B), 217.9 (s, 4C, *cis*-CO to B), 58.4 (s, 1C, C-(CH₃)₃), 33.6 (s, 3C, C-(CH₃)₃), 3.3 (s, 3C, Si-(CH₃)₃). ¹³C{¹H}-DEPT135 NMR (125.77 MHz, C₆D₆, 297 K) [ppm]: δ = 33.6 (s, 3C, C-(CH₃)₃), 3.3 (s, 3C, Si-(CH₃)₃). ¹¹B{¹H} NMR (160.47 MHz, C₆D₆, BF₃.OEt₂, 297 K) [ppm]: δ = 97.0 (br s). ²⁹Si{¹H} NMR (79.49 MHz, C₆D₆, SiMe₄, 297 K) [ppm]: δ = 3.4 (s). IR (solid)

[cm^{-1}]: $\nu = 3255, 2981, 2058, 1969, 1900, 1383, 1255, 1171$. **EA** [%]: calculated for $\text{C}_{12}\text{H}_{18}\text{BCrNO}_5\text{Si}$: C 41.52, H 5.23, N 4.03; found: C 41.58, H 5.25, N 3.93. **DTA** [$^{\circ}\text{C}$]: mp = 60, decomp. ≥ 211 .

Synthesis of $[(\text{OC})_5\text{Mo}\{\text{BN}(\text{SiMe}_3)(t\text{Bu})\}]$ (1b**).** A solution of $[(\text{OC})_5\text{Mo}(\text{NMe}_3)]$ (0.93 g, 3.2 mmol) in THF (5 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and a solution of $\text{Na}[\text{C}_{10}\text{H}_8]$ (32 mL, 0.20 M in THF) was added dropwise over a period of 10 min. After the addition was completed, all volatile materials were removed under high vacuum ($0\text{ }^{\circ}\text{C}/0.001\text{ Torr}$) and the remaining brown/yellow solids were dissolved in Et_2O (20 mL) and triturated in an ultrasonic bath for 2 min to extract the remaining naphthalene from the crude material. The reaction mixture was separated by centrifugation to concentrate $\text{Na}_2[\text{Mo}(\text{CO})_5]$ as a yellow solid with a Et_2O supernatant. The supernatant was subsequently decanted and the process repeated two additional times (2 x 20 mL Et_2O) in order to remove residual naphthalene. The remaining solid precipitate was dried briefly to yield $\text{Na}_2[\text{Mo}(\text{CO})_5]$ as a light brown/yellow powder. This powder was suspended in toluene and cooled to $-78\text{ }^{\circ}\text{C}$ after which $\text{Br}_2\text{BN}(\text{SiMe}_3)(t\text{Bu})$ (1.00 g, 3.17 mmol) was added dropwise by syringe. The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for one hour after which the color of the reaction mixture changed from light yellow to dark brown. The reaction flask was subsequently removed from the cold bath and allowed to stir for an additional hour while slowly warming to room temperature. Over the course of this additional hour the reaction mixture changed to a completely opaque black suspension. All volatiles were then removed under high vacuum and the black solids were dissolved in pentane (20 mL). This pentane suspension was triturated in an ultrasonic bath for a period of 2 min and separated by centrifugation to concentrate the salt elimination byproduct from a black pentane supernatant. Filtration of the supernatant yielded a black pentane fraction, which precipitated colorless crystalline solids upon storage in the $-78\text{ }^{\circ}\text{C}$ freezer after a period of 24 h. These colorless crystalline solids correspond to a crude sample of $[(\text{OC})_5\text{Mo}\{\text{BN}(\text{SiMe}_3)(t\text{Bu})\}]$, which could be further purified by redissolving the crude material in pentane and storage at $-78\text{ }^{\circ}\text{C}$ for an additional period of 24 h. Removal of the supernatant from the subsequent crystalline material and drying of the product under high vacuum yielded analytically pure $[(\text{OC})_5\text{Mo}\{\text{BN}(\text{SiMe}_3)(t\text{Bu})\}]$ (0.080 g, 0.21 mmol) in $<10\%$ yield. Crystals suitable for X-ray diffraction were grown from saturated solutions of $[(\text{OC})_5\text{Mo}\{\text{BN}(\text{SiMe}_3)(t\text{Bu})\}]$ in hexane. **^1H NMR** (500.13 MHz, C_6D_6 , 297 K) [ppm]: $\delta = 1.14$ (s, 9H, C- $(\text{CH}_3)_3$), 0.14 (s, 9H, Si- $(\text{CH}_3)_3$, $^2J_{\text{H-Si}} = 6.6\text{ Hz}$). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (125.77 MHz, C_6D_6 , 297 K) [ppm]: $\delta = 207.5$ (s, 4C, *cis*-CO to B), 206.9 (s, 1C, *trans*-CO to B), 58.3 (s, 1C, C- $(\text{CH}_3)_3$), 33.9 (s, 3C, C- $(\text{CH}_3)_3$), 3.5 (s, 3C, Si- $(\text{CH}_3)_3$). **$^{13}\text{C}\{^1\text{H}\}$ -DEPT135 NMR** (125.77 MHz, C_6D_6 , 297 K) [ppm]: $\delta = 33.9$ (s, 3C, C- $(\text{CH}_3)_3$), 3.5 (s, 3C, Si- $(\text{CH}_3)_3$). **$^{11}\text{B}\{^1\text{H}\}$ NMR** (160.47 MHz, C_6D_6 , $\text{BF}_3\cdot\text{OEt}_2$, 297 K) [ppm]: $\delta = 95.7$ (br s). **$^{29}\text{Si}\{^1\text{H}\}$ NMR** (79.49 MHz, C_6D_6 , SiMe_4 , 297 K) [ppm]: δ

= 3.4 (s). IR (solid) [cm⁻¹]: ν = 2981, 2065, 1896, 1383, 1254, 1171. EA [%]: calculated for C₁₂H₁₈BMoNO₅Si: C 36.85, H 4.64, N 3.58; found: C 36.98, H 4.64, N 3.62. DTA [°C]: decomp. \geq r.t.

Synthesis of [(OC)₅W{BN(SiMe₃)(tBu)}] (1c). A solution of [(OC)₅W(NMe₃)] [(OC)₅Mo(NMe₃)] (0.67 g, 1.8 mmol) in THF (5 mL) was cooled to -78 °C and a solution of Na[C₁₀H₈] (18 mL, 0.20 M in THF) was added dropwise over a period of 10 min. After the addition was completed, all volatile materials were removed under high vacuum (0 °C/0.001 Torr) and the remaining brown/yellow solids were dissolved in Et₂O (20 mL) and triturated in an ultrasonic bath for a period of 2 min to extract the remaining naphthalene from the crude material. The reaction mixture was separated by centrifugation to concentrate Na₂[W(CO)₅] as a yellow solid with an Et₂O supernatant. The supernatant was subsequently decanted and the process repeated two additional times (2 x 20 mL Et₂O) to remove residual naphthalene. The remaining solid precipitate was dried briefly to yield Na₂[W(CO)₅] as a light brown/yellow powder. This powder was suspended in toluene and cooled to -78 °C after which Br₂BN(SiMe₃)(tBu) (0.59 g, 1.9 mmol) was added dropwise by syringe. The reaction mixture was then stirred at -78 °C for one hour after which the color of the reaction mixture was witnessed to change from light yellow to dark brown. The reaction flask was removed from the cold bath and allowed to stir for an additional hour while slowly warming to room temperature. Over the course of this additional hour the reaction mixture changed to a completely opaque black suspension. All volatiles were then removed under high vacuum and the black solids were dissolved in pentane (20 mL). This pentane suspension was triturated in an ultrasonic bath for 2 min and separated by centrifugation to concentrate the salt elimination byproduct from a black pentane supernatant. Filtration of the supernatant yielded a black pentane fraction, which precipitated colorless crystalline solids upon storage at -78 °C after a period of 24 h. These colorless crystalline solids correspond to a crude fraction of [(OC)₅W{BN(SiMe₃)(tBu)}], which could be further purified by redissolving the crude material in pentane and storage in a -78 °C freezer for an additional 24 h. Removal of the supernatant from the subsequent crystalline material and drying of the product under high vacuum yielded analytically pure [(OC)₅W{BN(SiMe₃)(tBu)}] (0.293 g, 0.612 mmol) in 35% yield. Crystals suitable for X-ray diffraction were grown from saturated solutions of [(OC)₅W{BN(SiMe₃)(tBu)}] in hexane. ¹H NMR (500.13 MHz, C₆D₆, 297 K) [ppm]: δ = 1.14 (s, 9H, C-(CH₃)₃), 0.15 (s, 9H, Si-(CH₃)₃, ²J_{H-Si} = 6.8 Hz). ¹³C{¹H} NMR (125.77 MHz, C₆D₆, 297 K) [ppm]: δ = 197.7 (s, 4C, *cis*-CO to B, ¹J_{C-W} = 121 Hz), 191.2 (s, 1C, *trans*-CO to B, ¹J_{C-W} = 126 Hz), 58.0 (s, 1C, C-(CH₃)₃), 34.0 (s, 3C, C-(CH₃)₃), 3.5 (s, 3C, Si-(CH₃)₃). ¹³C{¹H}-DEPT135 NMR (125.77 MHz, C₆D₆, 297 K) [ppm]: δ = 34.0 (s, 3C, C-(CH₃)₃), 3.50 (s, 3C, Si-(CH₃)₃). ¹¹B{¹H} NMR (160.47 MHz, C₆D₆, BF₃.OEt₂, 297 K) [ppm]: δ = 91.7 (br s). ²⁹Si{¹H} NMR (79.49 MHz, C₆D₆, SiMe₄, 297 K) [ppm]: δ = 2.5 (s). IR (solid) [cm⁻¹]: ν = 3735, 3053, 2985, 2065, 1898, 1441, 1369, 1254, 1167. EA [%]:

calculated for $C_{12}H_{18}BWO_5Si$: C 30.09, H 3.79, N 2.92; found: C 29.72, H 3.46, N 2.79. **DTA** [$^{\circ}C$]: mp = 73, endo. = 150, decomp. \geq 233.

Synthesis of $[(\eta^5-C_5H_5)(OC)_3V\{BN(SiMe_3)(tBu)\}]$ (2). A solution of $[(OC)_5W\{BN(SiMe_3)(tBu)\}]$ (45 mg, 0.096 mmol) and $[(\eta^5-C_5H_5)V(CO)_4]$ (23 mg, 0.10 mmol) in benzene was irradiated with a high-pressure Hg lamp at room temperature for approximately 14 h. After completion of the reaction was ascertained *via* monitoring by $^{11}B\{^1H\}$ NMR spectroscopy, all volatiles were removed under high vacuum (0.001 Torr). The resulting solid material was redissolved in hexamethyldisiloxane and filtered through a column (0.5 x 2.0 cm) of pacified silica gel.⁶ Storage of this filtered solution at $-30^{\circ}C$ for a week yielded $[(\eta^5-C_5H_5)(OC)_3V\{BN(SiMe_3)(tBu)\}]$ as an orange crystalline solid. The supernatant was subsequently decanted and the crystalline material dried under vacuum to give $[(\eta^5-C_5H_5)(OC)_3V\{BN(SiMe_3)(tBu)\}]$ (29 mg, 0.081 mmol) in 84% yield. Crystals suitable for X-ray diffraction were grown from saturated solutions of $[(\eta^5-C_5H_5)(OC)_3V\{BN(SiMe_3)(tBu)\}]$ in hexane. **1H NMR** (500.13 MHz, C_6D_6 , 297 K) [ppm]: δ = 4.64 (s, 5H, $\eta^5-C_5H_5$), 1.37 (s, 9H, C-(CH_3)₃), 0.26 (s, 9H, Si-(CH_3)₃), $^2J_{H-Si}$ = 6.7 Hz). **$^{13}C\{^1H\}$ NMR** (125.77 MHz, C_6D_6 , 297 K) [ppm]: δ = 197.7 (s, 3C, C-O), 91.3 (s, 5C, $\eta^5-C_5H_5$), 57.8 (s, 1C, C-(CH_3)₃), 33.1 (s, 3C, C-(CH_3)₃), 2.8 (s, 3C, Si-(CH_3)₃), $^1J_{C-Si}$ = 58 Hz). **$^{13}C\{^1H\}$ -DEPT135 NMR** (125.77 MHz, C_6D_6 , 297 K) [ppm]: δ = 91.3 (s, 5C, $\eta^5-C_5H_5$), 33.1 (s, 3C, C-(CH_3)₃), 2.8 (s, 3C, Si-(CH_3)₃). **$^{11}B\{^1H\}$ NMR** (160.47 MHz, C_6D_6 , $BF_3 \cdot OEt_2$, 297 K) [ppm]: δ = 100.3 (br s). **$^{29}Si\{^1H\}$ NMR** (79.49 MHz, C_6D_6 , $SiMe_4$, 297 K) [ppm]: δ = 3.6 (s). **EA** [%]: calculated for $C_{15}H_{23}BNO_3SiV$: C 50.72, H 6.53, N 3.94; found: C 46.98, H 6.30, N 3.40. **DTA** [$^{\circ}C$]: mp = 74, decomp. \geq 259.

Synthesis of $\{[(\eta^5-C_5H_5)Ni]_2(\mu-CO)\{\mu-BN(SiMe_3)(tBu)\}\}$ (3). A solution of $[(\eta^5-C_5H_5)_2Ni_2(CO)_2]$ (16 mg, 0.054 mmol) and $[(OC)_5W\{BN(SiMe_3)(tBu)\}]$ (27 mg, 0.056 mmol) in hexane (2 mL) was irradiated with a high-pressure Hg lamp at room temperature for approximately 7 h. After completion of the reaction was ascertained *via* monitoring by $^{11}B\{^1H\}$ NMR spectroscopy, all volatiles were removed under high vacuum (0.001 Torr). The resulting solid material was redissolved in hexamethyldisiloxane and filtered through a column (0.5 x 2.0 cm) of pacified silica gel.⁶ Storage of this filtered solution at $-30^{\circ}C$ for a week yielded $\{[(\eta^5-C_5H_5)Ni]_2(\mu-CO)\{\mu-BN(SiMe_3)(tBu)\}\}$ as a dark red crystalline solid. The supernatant was subsequently decanted and the crystalline material dried under vacuum to give $\{[(\eta^5-C_5H_4Me)Co]_2(\mu-CO)\{\mu-BN(SiMe_3)(tBu)\}\}$ (17 mg, 0.040 mmol) in 74% yield. Crystals suitable for X-ray diffraction were grown from saturated solutions of $\{[(\eta^5-C_5H_5)Ni]_2(\mu-CO)\{\mu-BN(SiMe_3)(tBu)\}\}$ in hexane. **1H NMR** (500.13 MHz, C_6D_6 , 297 K) [ppm]: δ = 5.32 (s, 10H, $\eta^5-C_5H_5$), 1.18 (s, 9H, C-(CH_3)₃), 0.24 (s, 9H, Si-(CH_3)₃), $^2J_{H-Si}$ = 6.6 Hz). **$^{13}C\{^1H\}$ NMR** (125.77 MHz, C_6D_6 , 297 K) [ppm]: δ = 92.5 (s, 10C, $\eta^5-C_5H_5$), 56.9 (s, 1C, C-(CH_3)₃), 33.2 (s, 3C, C-(CH_3)₃), 4.0 (s, 3C, Si-(CH_3)₃), $^1J_{C-Si}$ = 57 Hz). **$^{13}C\{^1H\}$**

DEPT135 NMR (125.77 MHz, C₆D₆, 297 K) [ppm]: δ = 92.5 (s, 10C, η^5 -C₅H₅), 33.2 (s, 3C, C-(CH₃)₃), 4.0 (s, 3C, Si-(CH₃)₃). **¹¹B{¹H} NMR** (160.47 MHz, C₆D₆, BF₃.OEt₂, 297 K) [ppm]: δ = 94.1 (br s). **²⁹Si{¹H} NMR** (79.49 MHz, C₆D₆, SiMe₄, 297 K) [ppm]: δ = -2.8 (s). **IR** (solid) [cm⁻¹]: ν = 3248, 2968, 2085, 2002, 1817, 1541, 1469, 1392, 1360, 1317, 1252. **EA** [%]: calculated for C₁₈H₂₈BNNi₂OSi: C 50.20, H 6.55, N 3.25; found: C 50.29, H 6.62, N 3.20. **DTA** [°C]: mp = 114, decomp. \geq 235.

Synthesis of [({ η^5 -C₅H₄Me)Co}₂{ μ -(CO)}₂{ μ -BN(SiMe₃)(tBu)}] (4). A solution of [({ η^5 -C₅H₄Me)Co(CO)₂] (42 mg, 0.22 mmol) and [(OC)₅Cr{BN(SiMe₃)(tBu)}] (30 mg, 0.086 mmol) in hexane (2 mL) was irradiated with a high-pressure Hg lamp at room temperature for approximately 8 h. Monitoring of the reaction mixture was undertaken *via* ¹¹B{¹H} NMR spectroscopy which showed the formation of two distinct products at δ = 81 ppm and δ = 104 ppm, which are proposed to correspond to the terminal and bridging borylene ligand coordination modes in solution. Once complete consumption of the [(OC)₅Cr{BN(SiMe₃)(tBu)}] was observed, irradiation was halted and all volatiles were removed under high vacuum (0.001 Torr). The resulting solid material was redissolved in hexamethyldisiloxane and filtered through a column (0.5 x 2.0 cm) of pacified silica gel.⁶ Storage of this filtered solution at -30 °C for a week yielded [({ η^5 -C₅H₄Me)Co}₂{ μ -(CO)}₂{ μ -BN(SiMe₃)(tBu)}] as a dark red crystalline solid. The supernatant was subsequently decanted and the crystalline material dried under vacuum to give [({ η^5 -C₅H₄Me)Co}₂{ μ -(CO)}₂{ μ -BN(SiMe₃)(tBu)}] (27 mg, 0.056 mmol) in 65% yield. Crystals suitable for X-ray diffraction were grown from saturated solutions of [({ η^5 -C₅H₄Me)Co}₂{ μ -(CO)}₂{ μ -BN(SiMe₃)(tBu)}] in hexane. **¹H NMR** (500.13 MHz, C₆D₆, 297 K) [ppm]: δ = 4.75 (s, 4H, η^5 -C₅H₄CH₃), 4.49 (s, 4H, η^5 -C₅H₄CH₃), 1.94 (s, 6H, η^5 -C₅H₄CH₃), 1.40 (s, 9H, C-(CH₃)₃), 0.34 (s, 9H, Si-(CH₃)₃). **¹³C{¹H} NMR** (125.77 MHz, C₆D₆, 297 K) [ppm]: δ = 103.2 (s, 2C, *ipso*-C of η^5 -C₅H₄CH₃), 88.6 (s, 4C, η^5 -C₅H₄CH₃), 88.3 (s, 4C, η^5 -C₅H₄CH₃), 56.8 (s, 1C, C-(CH₃)₃), 33.6 (s, 3C, C-(CH₃)₃), 13.2 (s, 2C, η^5 -C₅H₄CH₃), 5.9 (s, 3C, Si-(CH₃)₃, ¹J_{C-Si} = 57 Hz). **¹³C{¹H} DEPT135 NMR** (125.77 MHz, C₆D₆, 297 K) [ppm]: δ = 88.6 (s, 4C, η^5 -C₅H₄CH₃), 88.3 (s, 4C, η^5 -C₅H₄CH₃), 33.6 (s, 3C, C-(CH₃)₃), 13.2 (s, 2C, η^5 -C₅H₄CH₃), 5.9 (s, 3C, Si-(CH₃)₃, ¹J_{C-Si} = 57 Hz). **¹¹B{¹H} NMR** (160.47 MHz, C₆D₆, BF₃.OEt₂, 297 K) [ppm]: δ = 103.6 (br s). **²⁹Si{¹H} NMR** (79.49 MHz, C₆D₆, SiMe₄, 297 K) [ppm]: δ = -2.8 (s). **IR** (solid) [cm⁻¹]: ν = 3738, 2927, 2851, 2224, 1762, 1713, 1686, 1594, 1495, 1445, 1354, 1300, 1254. **EA** [%]: calculated for C₂₁H₃₂BCo₂NO₂Si: C 51.76, H 6.62, N 2.87; found: C 51.12, H 6.43, N 2.59.

Synthesis of [({ η^5 -C₅Me₅)Ir{BN(SiMe₃)(tBu)}₂] (5). A solution of [({ η^5 -C₅Me₅)Ir(CO)₂] (23 mg, 0.060 mmol) and [(OC)₅Cr{BN(SiMe₃)(tBu)}] (46 mg, 0.13 mmol) in hexane (2 mL) was irradiated with a high-pressure Hg lamp at room temperature for approximately 12 h. After completion of the reaction was ascertained *via* monitoring by ¹¹B{¹H} NMR spectroscopy, all volatiles were removed under high

vacuum (0.001 Torr). The resulting solid material was redissolved in hexamethyldisiloxane and filtered through a column (0.5 x 2.0 cm) of pacified silica gel.⁶ Storage of this filtered solution in the -30 °C freezer for a week yielded $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}\{\text{BN}(\text{SiMe}_3)(\text{tBu})\}_2]$ as a light yellow crystalline solid. The supernatant was subsequently decanted and the crystalline material dried under vacuum to give $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}\{\text{BN}(\text{SiMe}_3)(\text{tBu})\}_2]$ (22 mg, 0.035 mmol) in 58% yield. Crystals suitable for X-ray diffraction were grown from saturated solutions of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}\{\text{BN}(\text{SiMe}_3)(\text{tBu})\}_2]$ in hexane. **¹H NMR** (500.13 MHz, C₆D₆, 297 K) [ppm]: δ = 2.35 (s, 15H, $\eta^5\text{-C}_5(\text{CH}_3)_5$), 1.45 (s, 18H, C-(CH₃)₃), 0.44 (s, 18H, Si-(CH₃)₃, ²J_{H-Si} = 6.7 Hz). **¹³C{¹H} NMR** (125.77 MHz, C₆D₆, 297 K) [ppm]: δ = 94.7 (s, 5C, $\eta^5\text{-C}_5(\text{CH}_3)_5$), 52.0 (s, 2C, C-(CH₃)₃), 34.0 (s, 6C, C-(CH₃)₃), 11.8 (s, 5C, $\eta^5\text{-C}_5(\text{CH}_3)_5$), 4.5 (s, 6C, Si-(CH₃)₃, ¹J_{C-Si} = 57 Hz). **¹³C{¹H} DEPT135 NMR** (125.77 MHz, C₆D₆, 297 K) [ppm]: δ = 34.0 (s, 6C, C-(CH₃)₃), 11.8 (s, 5C, $\eta^5\text{-C}_5(\text{CH}_3)_5$), 4.5 (s, 6C, Si-(CH₃)₃). **¹¹B{¹H} NMR** (160.47 MHz, C₆D₆, BF₃·OEt₂, 297 K) [ppm]: δ = 70.8 (br s). **²⁹Si{¹H} NMR** (79.49 MHz, C₆D₆, SiMe₄, 297 K) [ppm]: δ = -1.2 (s). **IR** (solid) [cm⁻¹]: ν = 3749, 3249, 2964, 2897, 2002, 1653, 1408, 1363, 1252. **EA** [%]: calculated for C₂₄H₅₁B₂IrN₂Si₂: C 45.20, H 8.06, N 4.39; found: C 45.24, H 8.05, N 4.38. **DTA** [°C]: mp = 128, decomp. \geq 301.

Crystal Structure Determination

The crystal data were collected on a BRUKER X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $\text{Mo}_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,⁷ refined with the SHELXL program⁸ and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions.

The structures **1a**, **4**, and **5** showed disorder of $\text{N}(t\text{Bu})(\text{SiMe}_3)$ moiety (91:8, 89:11, and 50:50, respectively; two-fold axis). The N–Si and N–C distances were thus restrained (DFIX) using data obtained from a CSD search. As there are known structures of borylenes with $\text{N}(\text{SiMe}_3)_2$ groups, the accuracy of this parameter was higher, and thus the standard deviation used for this bond was set to 0.01. For the N–C distance no comparable borylenes are known and a general CSD search delivered a much wider range of bond lengths. Here we used a standard deviation of 0.02. For all disordered atoms the similarity restraint SIMU and rigid body restraint RIGU was applied to the atomic displacement parameters (ADP). The similarity of the N–C and N–Si distances in conjunction with the difference of structure factors of C/Si atoms caused problems with the refinement of the ADPs of silicon and tertiary carbon. Even the use of ADP constraints had no detectable influence on the resulting ellipsoids. Only an extremely small standard deviation value (<0.002) in the ISOR keyword (approximate isotropic behavior of listed atoms) led to reasonable shapes of both ellipsoids. All of the above con- and restraints were necessary to obtain physically meaningful and stable refinement. It can be assumed that these restraints have no large influence on the structural parameters of the rest of the molecule, but we still consider these data as proof of connectivity only.

Crystal data for $[(\text{OC})_5\text{Cr}\{\text{BN}(\text{SiMe}_3)(t\text{Bu})\}]$ (1a**; CCDC: 2032809):** $\text{C}_{12}\text{H}_{18}\text{BCrNO}_5\text{Si}$, $M_r = 347.17$, colourless plate, $0.30 \times 0.20 \times 0.09 \text{ mm}^3$, monoclinic space group $P2_1/n$, $a = 6.4770(15) \text{ \AA}$, $b = 13.825(2) \text{ \AA}$, $c = 19.041(3) \text{ \AA}$, $\beta = 93.196(8)^\circ$, $V = 1702.4(6) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.355 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 0.758 \text{ mm}^{-1}$, $F(000) = 720$, $T = 100(2) \text{ K}$, $R_1 = 0.0414$, $wR^2 = 0.0861$, 4599 independent reflections [$2\theta \leq 60.218^\circ$] and 227 parameters.

Crystal data for $[(\text{OC})_5\text{Mo}\{\text{BN}(\text{SiMe}_3)(t\text{Bu})\}]$ (1b**; CCDC: 2032810):** $\text{C}_{12}\text{H}_{18}\text{BMoNO}_5\text{Si}$, $M_r = 391.11$, colourless plate, $0.36 \times 0.22 \times 0.06 \text{ mm}^3$, monoclinic space group $P2_1/c$, $a = 15.031(4) \text{ \AA}$, $b = 6.6210(14) \text{ \AA}$, $c = 18.182(4) \text{ \AA}$, $\beta = 105.893(12)^\circ$, $V = 1740.4(7) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.493 \text{ g}\cdot\text{cm}^{-3}$,

$\mu = 0.838 \text{ mm}^{-1}$, $F(000) = 792$, $T = 100(2) \text{ K}$, $R_1 = 0.0348$, $wR^2 = 0.0610$, 5423 independent reflections [$2\theta \leq 65.344^\circ$] and 196 parameters.

Crystal data for [(OC)₅W{BN(SiMe₃)(tBu)}] (1c; CCDC: 2032811): C₁₂H₁₈BNO₅SiW, $M_r = 479.02$, colourless block, 0.50×0.32×0.20 mm³, monoclinic space group $P2_1/c$, $a = 14.971(4) \text{ \AA}$, $b = 6.5880(18) \text{ \AA}$, $c = 18.181(4) \text{ \AA}$, $\beta = 106.059(9)^\circ$, $V = 1723.2(7) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.846 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 6.789 \text{ mm}^{-1}$, $F(000) = 920$, $T = 100(2) \text{ K}$, $R_1 = 0.0210$, $wR^2 = 0.0399$, 5446 independent reflections [$2\theta \leq 65.968^\circ$] and 196 parameters.

Crystal data for [(\eta⁵-C₅H₅)(OC)₃V{BN(SiMe₃)(tBu)}] (2; CCDC: 2032812): C₁₅H₂₃BNO₃SiV, $M_r = 355.18$, yellow block, 0.33×0.24×0.084 mm³, orthorhombic space group $Pbca$, $a = 13.380(5) \text{ \AA}$, $b = 13.438(5) \text{ \AA}$, $c = 19.996(7) \text{ \AA}$, $V = 3595(2) \text{ \AA}^3$, $Z = 8$, $\rho_{\text{calcd}} = 1.312 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 0.628 \text{ mm}^{-1}$, $F(000) = 1488$, $T = 100(2) \text{ K}$, $R_1 = 0.0280$, $wR^2 = 0.0640$, 3843 independent reflections [$2\theta \leq 53.832^\circ$] and 205 parameters.

Crystal data for [(\eta⁵-C₅H₅)Ni]₂(μ-CO){μ-BN(SiMe₃)(tBu)}] (3; polymorph 1; CCDC: 2032813): C₁₈H₂₈BNNi₂OSi, $M_r = 430.73$, yellow block, 0.30×0.15×0.08 mm³, monoclinic space group $P2_1/c$, $a = 12.436(3) \text{ \AA}$, $b = 9.8525(18) \text{ \AA}$, $c = 16.497(3) \text{ \AA}$, $\beta = 96.081(14)^\circ$, $V = 2010.0(7) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.423 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 1.937 \text{ mm}^{-1}$, $F(000) = 904$, $T = 100(2) \text{ K}$, $R_1 = 0.0533$, $wR^2 = 0.0970$, 6217 independent reflections [$2\theta \leq 65.564^\circ$] and 223 parameters. **Crystal data for [(\eta⁵-C₅H₅)Ni]₂(μ-CO){μ-BN(SiMe₃)(tBu)}] (3; polymorph 2; CCDC 2032815):** C₁₈H₂₈BNNi₂OSi, $M_r = 430.73$, yellow plate, 0.10×0.06×0.03 mm³, monoclinic space group $C2/c$, $a = 26.480(10) \text{ \AA}$, $b = 9.257(3) \text{ \AA}$, $c = 16.494(8) \text{ \AA}$, $\beta = 100.343(8)^\circ$, $V = 3977(3) \text{ \AA}^3$, $Z = 8$, $\rho_{\text{calcd}} = 1.439 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 1.958 \text{ mm}^{-1}$, $F(000) = 1808$, $T = 100(2) \text{ K}$, $R_1 = 0.0824$, $wR^2 = 0.0888$, 5543 independent reflections [$2\theta \leq 59.334^\circ$] and 223 parameters.

Crystal data for [(\eta⁵-C₅H₄Me)Co]₂(μ-CO)₂{μ-BN(SiMe₃)(tBu)}] (4; CCDC: 2032816): C₂₁H₃₂BCo₂NO₂Si, $M_r = 487.23$, red block, 0.12×0.075×0.035 mm³, monoclinic space group $C2/c$, $a = 16.269(12) \text{ \AA}$, $b = 9.827(7) \text{ \AA}$, $c = 16.702(12) \text{ \AA}$, $\beta = 123.96(2)^\circ$, $V = 2215(3) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.461 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 1.568 \text{ mm}^{-1}$, $F(000) = 1016$, $T = 100(2) \text{ K}$, $R_1 = 0.0597$, $wR^2 = 0.1322$, 2847 independent reflections [$2\theta \leq 62.33^\circ$] and 155 parameters.

Crystal data for [(\eta⁵-C₅Me₅)Ir{BN(SiMe₃)(tBu)}₂] (5; CCDC: 2032817): C₂₄H₅₁B₂IrN₂Si₂, $M_r = 637.66$, colourless block, 0.32×0.19×0.17 mm³, monoclinic space group $P2_1/n$, $a = 8.443(4) \text{ \AA}$,

$b = 35.377(19) \text{ \AA}$, $c = 10.387(5) \text{ \AA}$, $\beta = 97.236(14)^\circ$, $V = 3078(3) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.376 \text{ g}\cdot\text{cm}^{-3}$,
 $\mu = 4.429 \text{ mm}^{-1}$, $F(000) = 1296$, $T = 100(2) \text{ K}$, $R_1 = 0.0332$, $wR^2 = 0.0565$, 8815 independent reflections
[$2\theta \leq 61.832^\circ$] and 328 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-2032809 (**1a**), 2032810 (**1b**), 2032811 (**1c**), 2032812 (**2**), 2032813 (**3**; polymorph 1), 2032815 (**3**; polymorph 2), 2032816 (**4**), 2032817 (**5**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

NMR Spectra

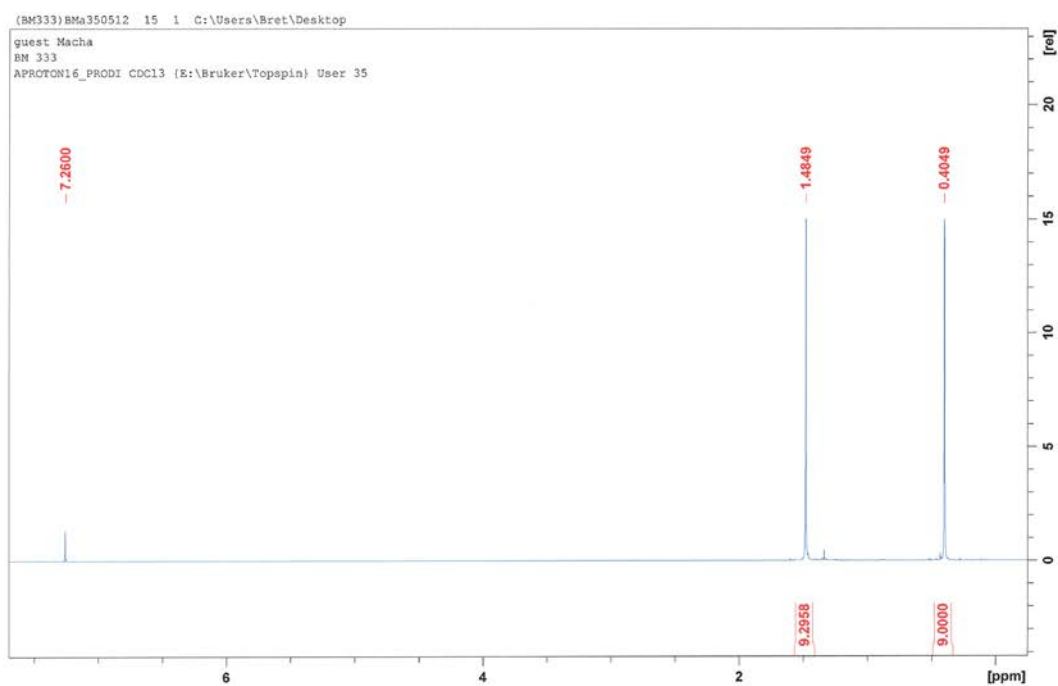


Fig. S1. ^1H NMR spectrum of $\text{Br}_2\text{BN}(\text{SiMe}_3)(\text{tBu})$ in CDCl_3 at RT

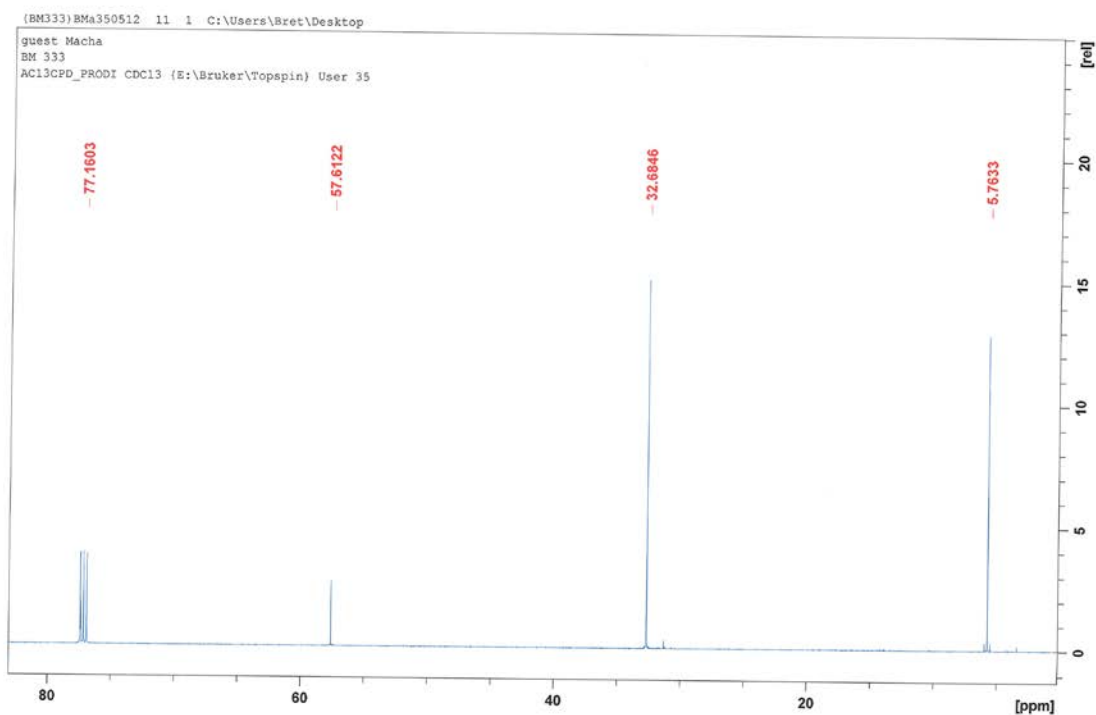


Fig. S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Br}_2\text{BN}(\text{SiMe}_3)(\text{tBu})$ in CDCl_3 at RT

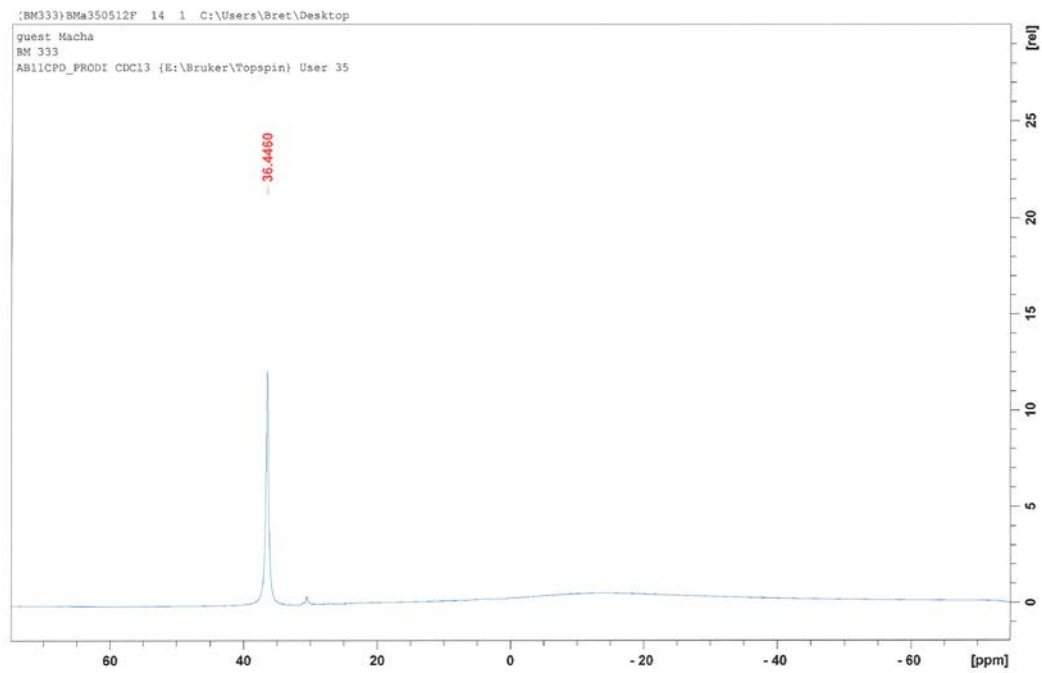


Fig. S3. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of $\text{Br}_2\text{BN}(\text{SiMe}_3)(t\text{Bu})$ in CDCl_3 at RT

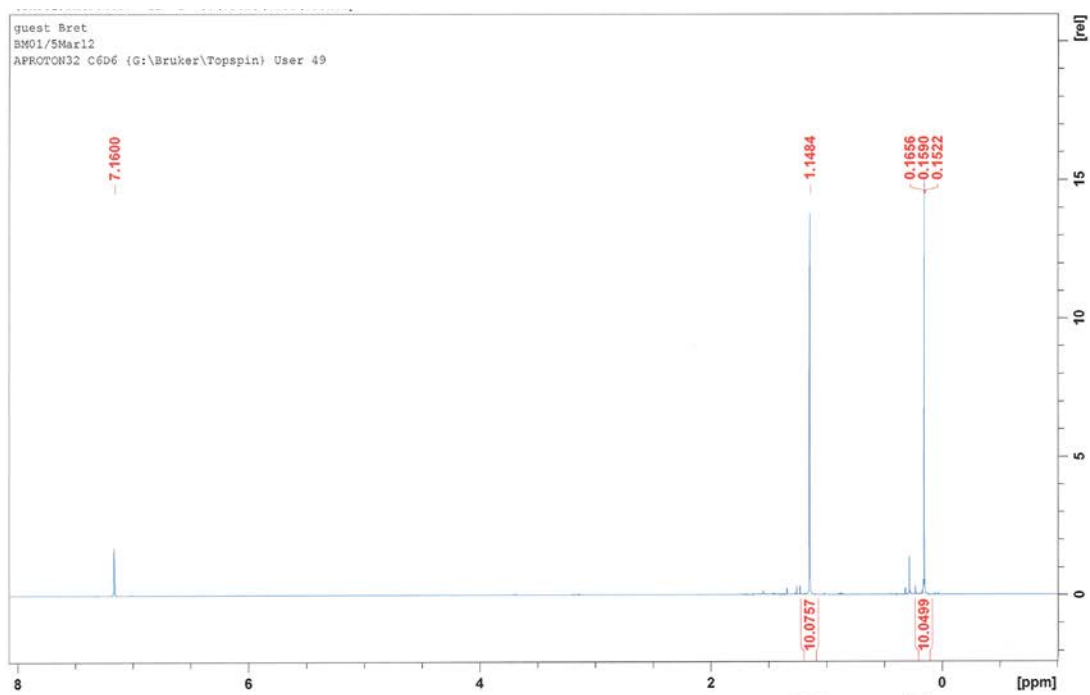


Fig. S4. ^1H NMR spectrum of **1a** in C_6D_6 at RT

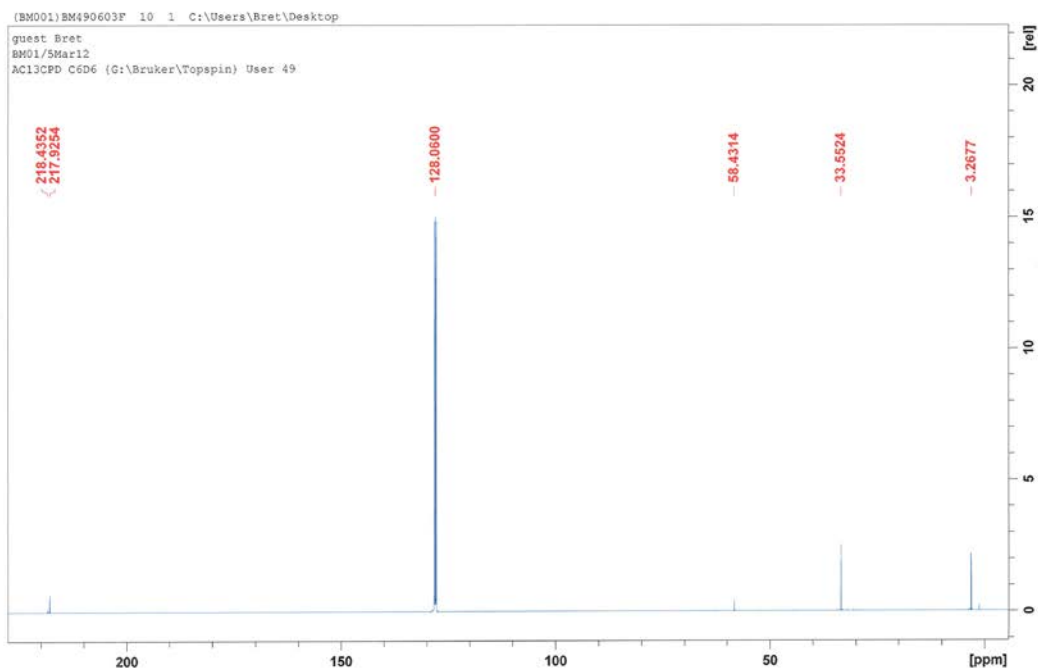


Fig. S5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1a** in C_6D_6 at RT.

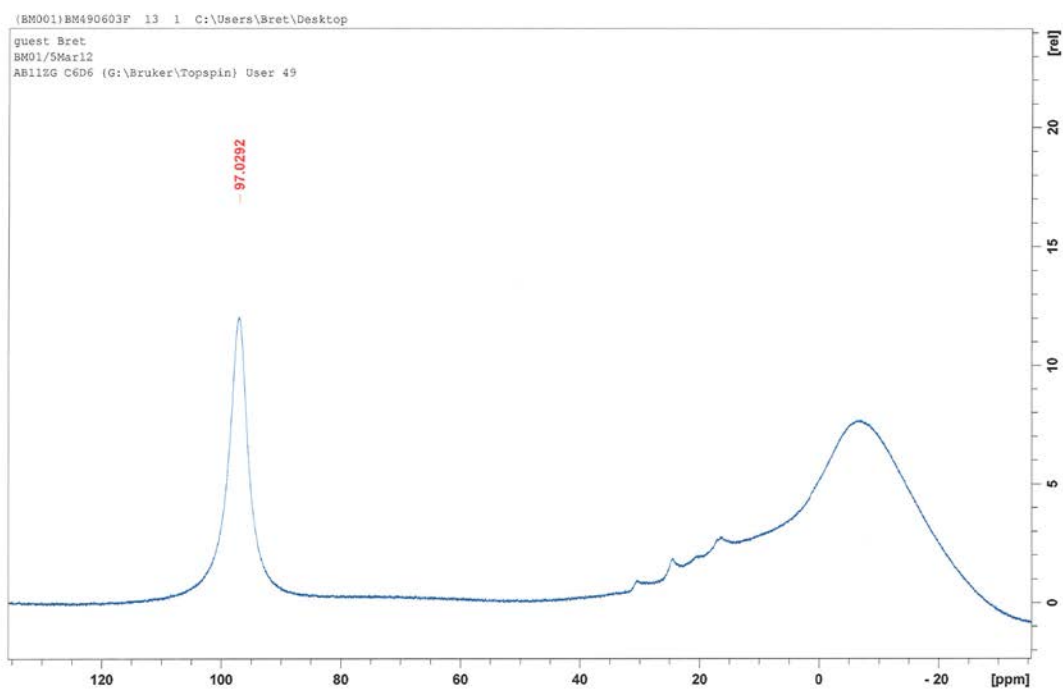


Fig. S6. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **1a** in C_6D_6 at RT.

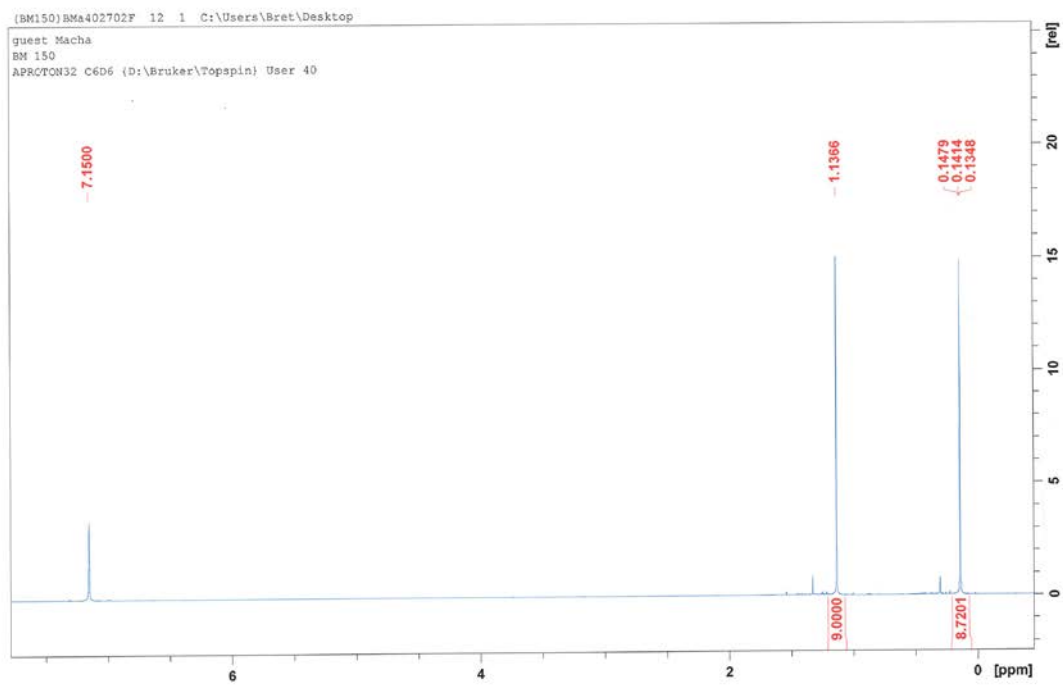


Fig. S7. ^1H NMR spectrum of **1b** in C_6D_6 at RT.

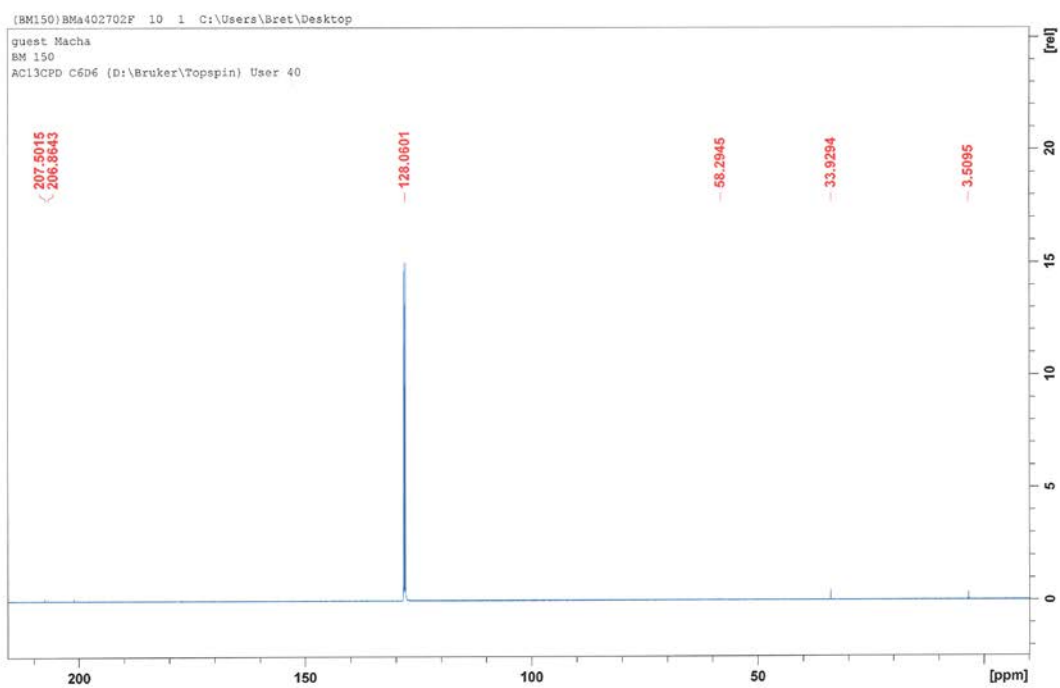


Fig. S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1b** in C_6D_6 at RT.

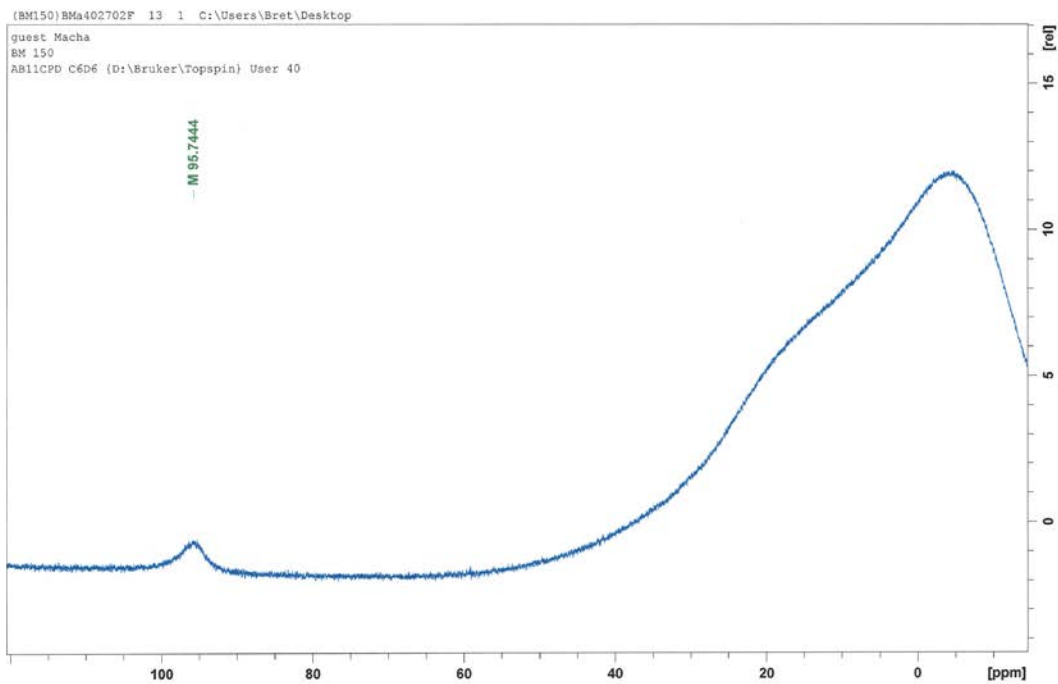


Fig. S9. ^{11}B $\{^1\text{H}\}$ NMR spectrum of **1b** in C_6D_6 at RT.

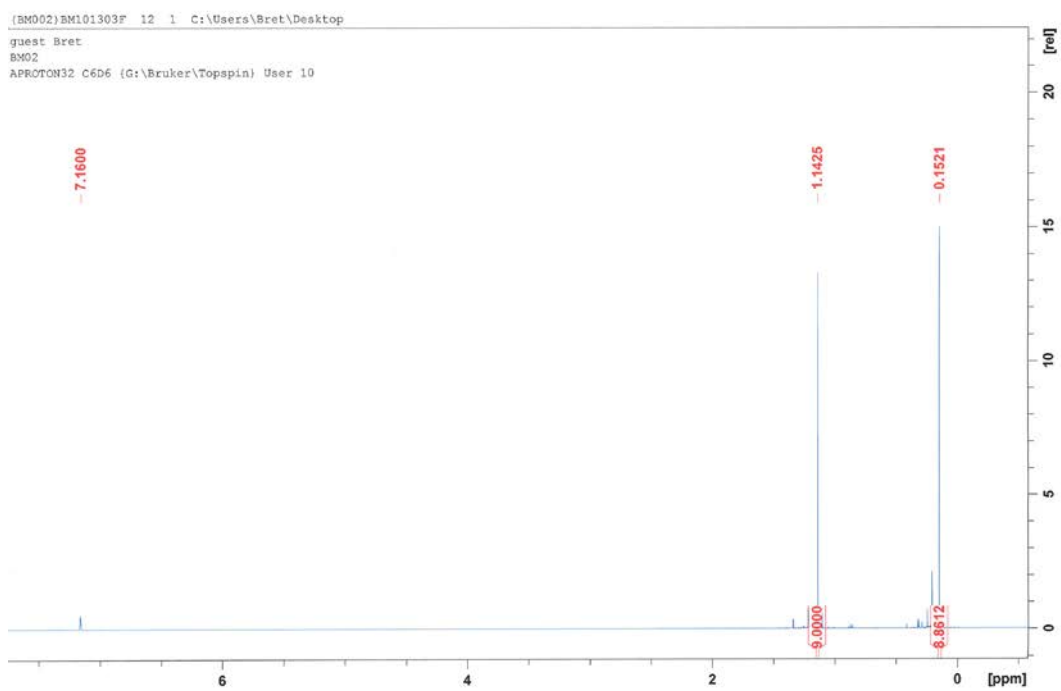


Fig. S10. ^1H NMR spectrum of **1c** in C_6D_6 at RT.

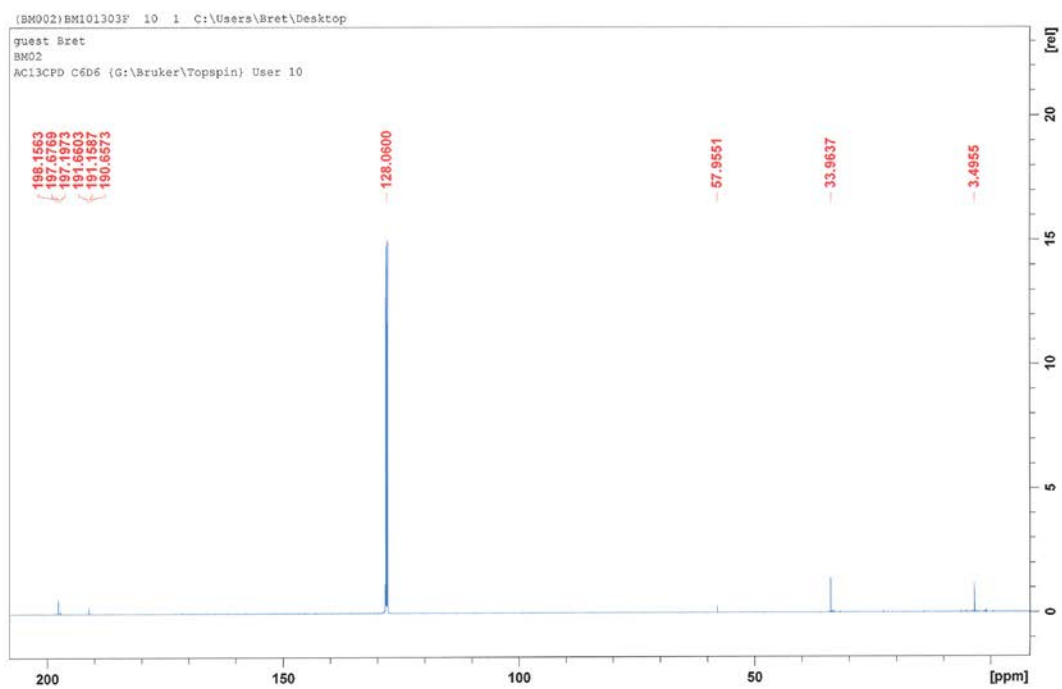


Fig. S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1c** in C_6D_6 at RT.

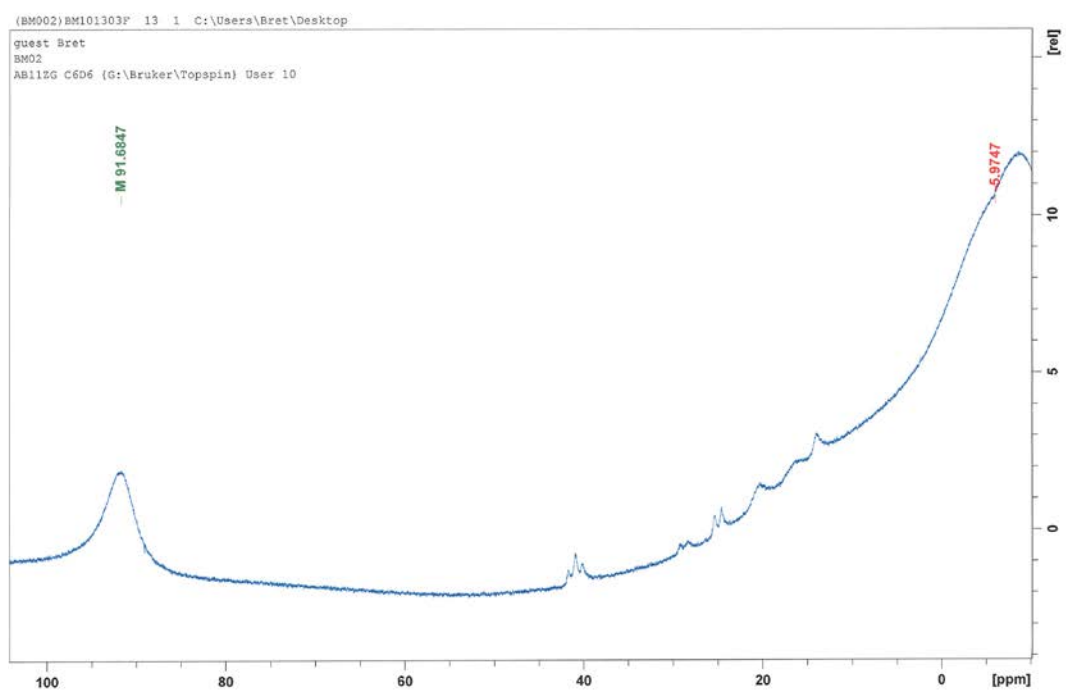


Fig. S12. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **1c** in C_6D_6 at RT.

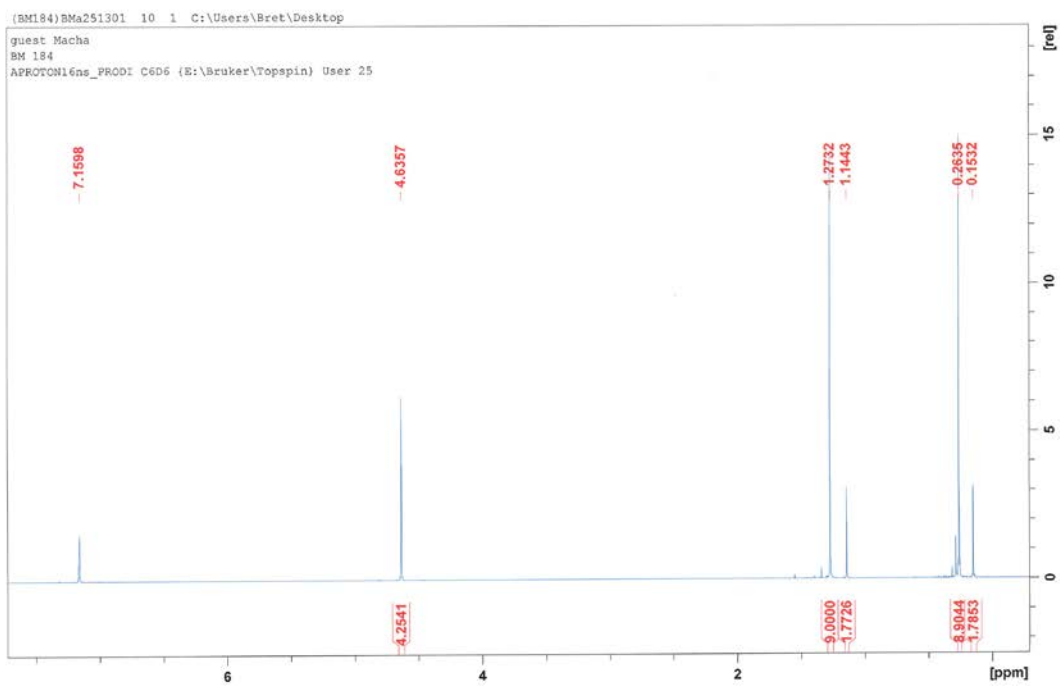


Fig. S13. ^1H NMR spectrum of **2** in C_6D_6 at RT.

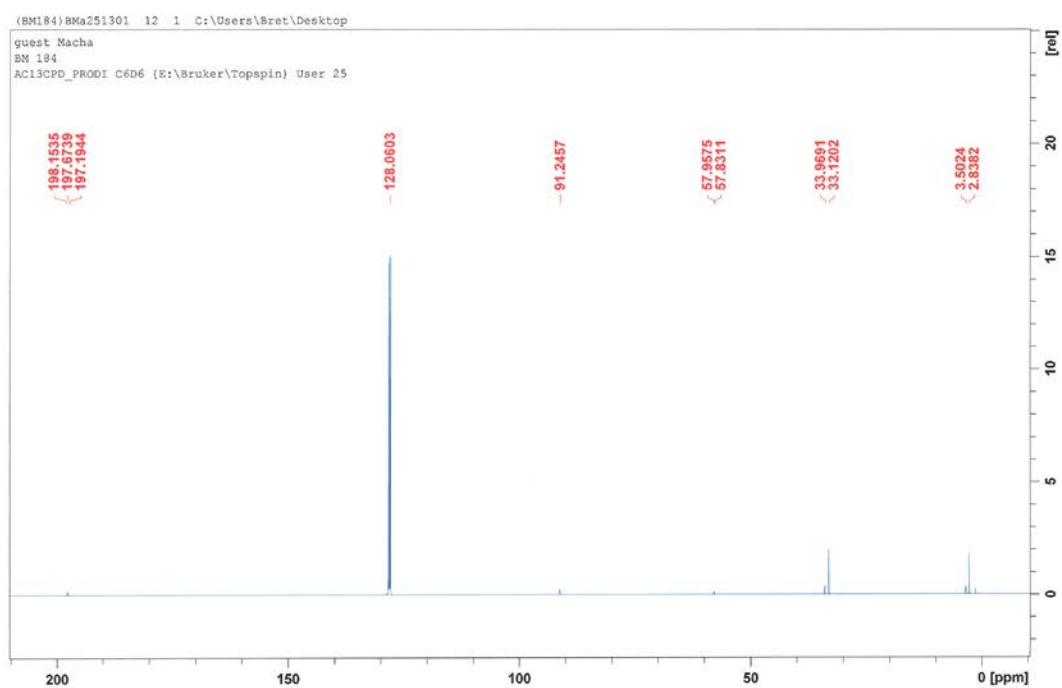


Fig. S14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** in C_6D_6 at RT.

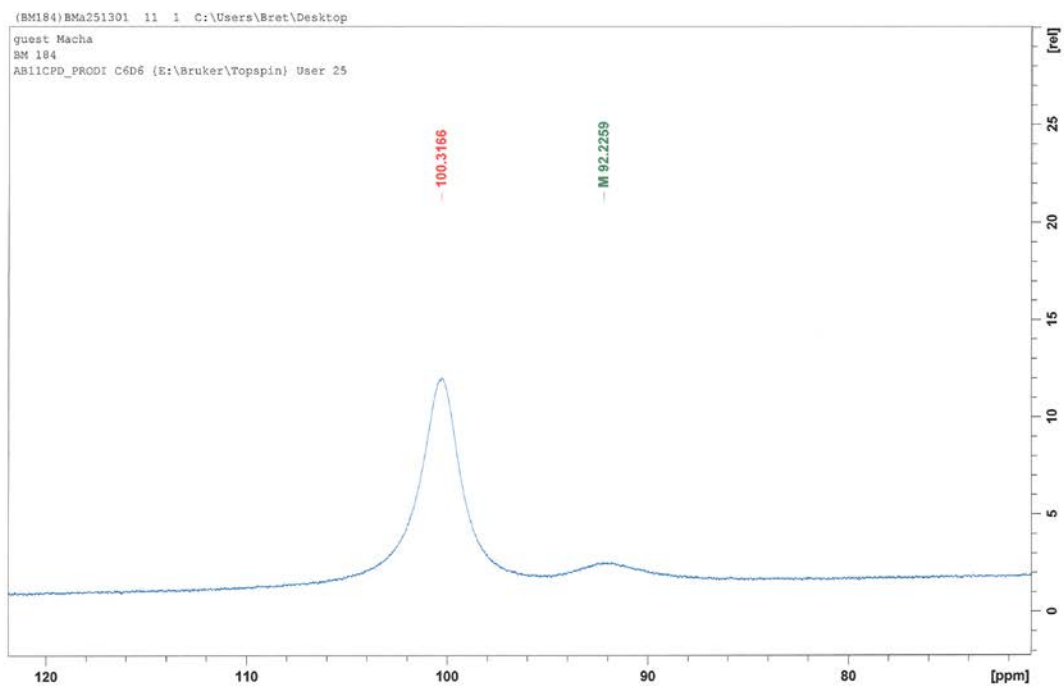


Fig. S15. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **2** in C_6D_6 at RT.

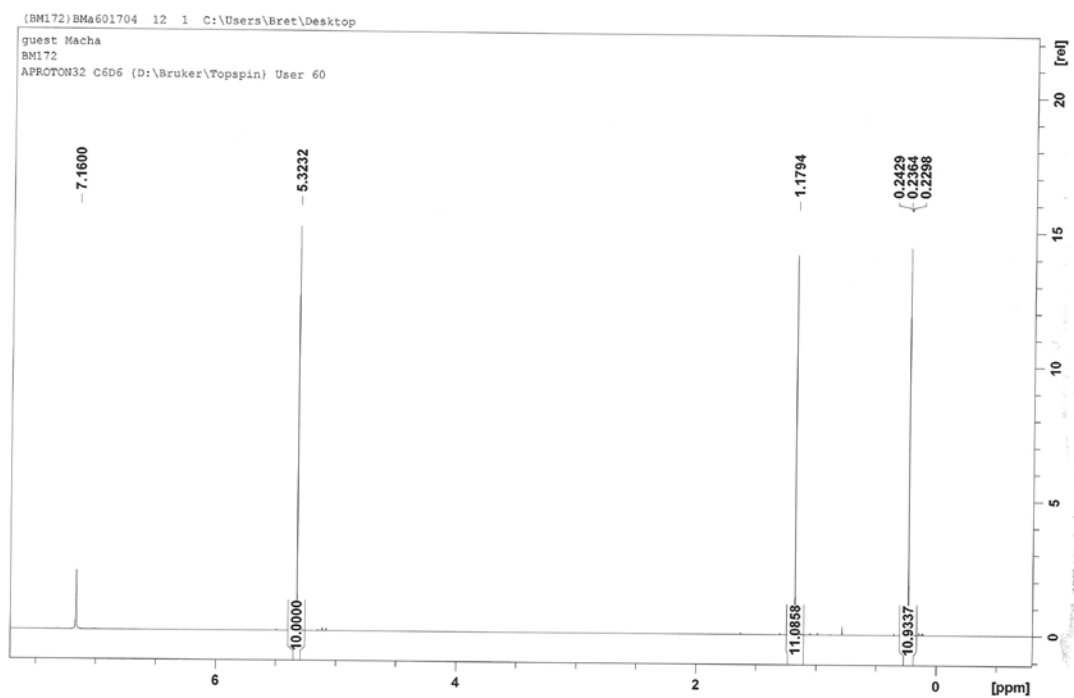


Fig. S16. ^1H NMR spectrum of **3** in C_6D_6 at RT.

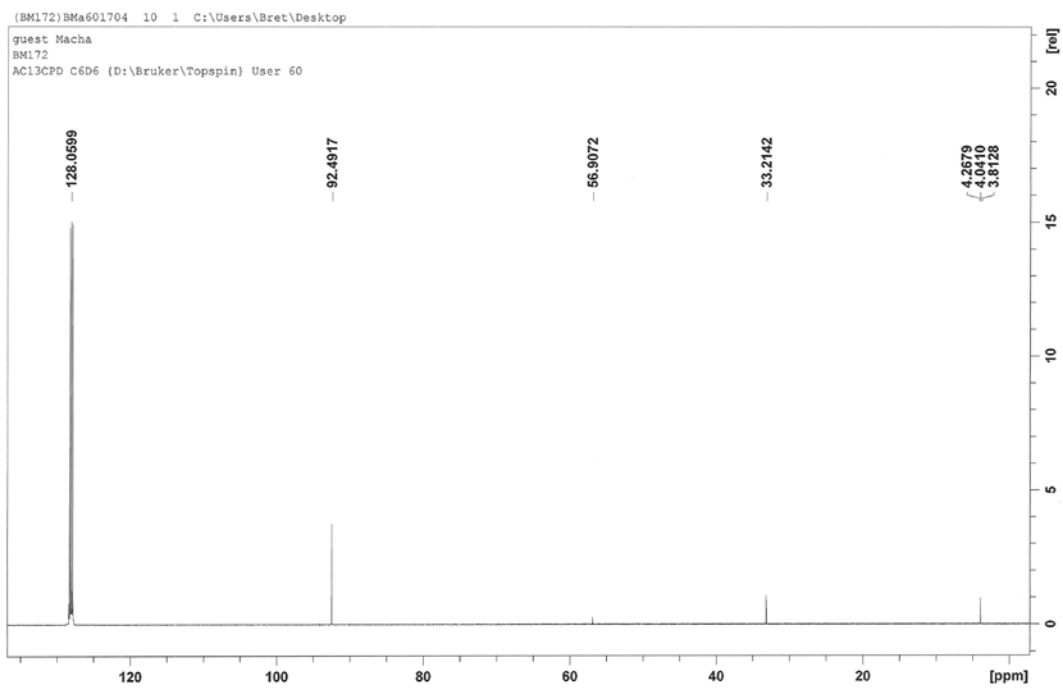


Fig. S17. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** in C_6D_6 at RT.

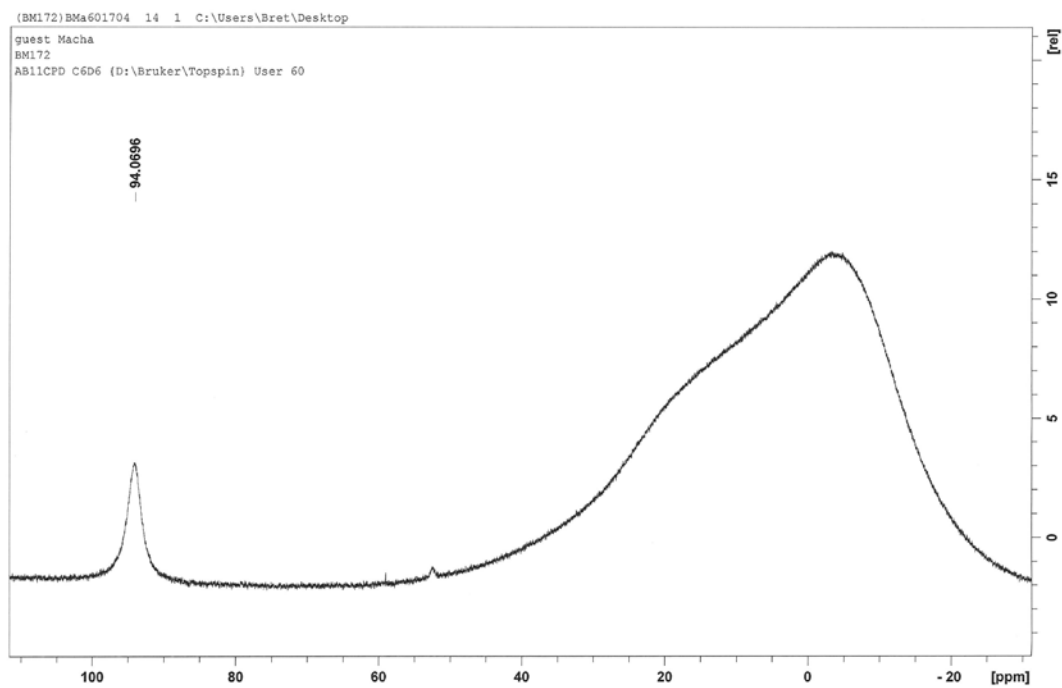


Fig. S18. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **3** in C_6D_6 at RT.

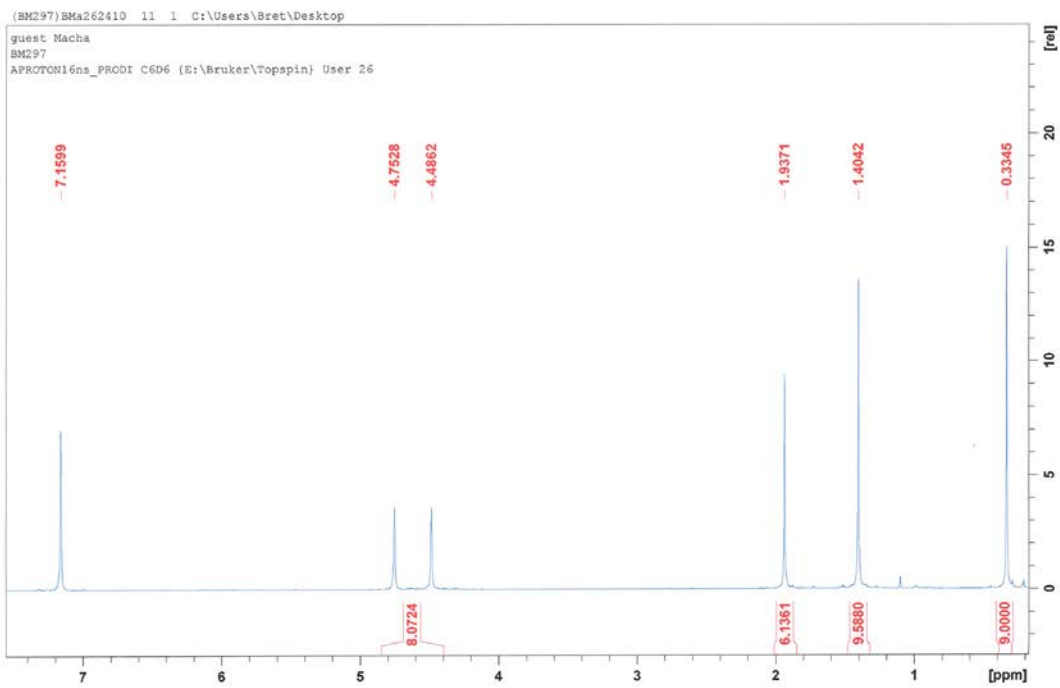


Fig. S19. ^1H NMR spectrum of **4** in C_6D_6 at RT.

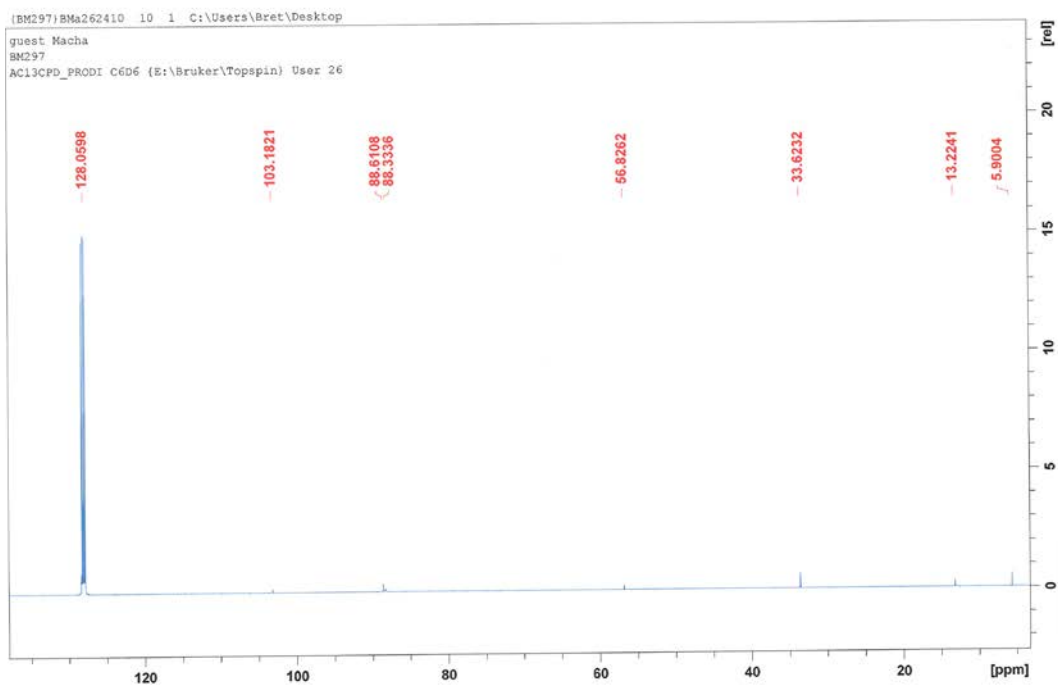


Fig. S20. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4** in C_6D_6 at RT.

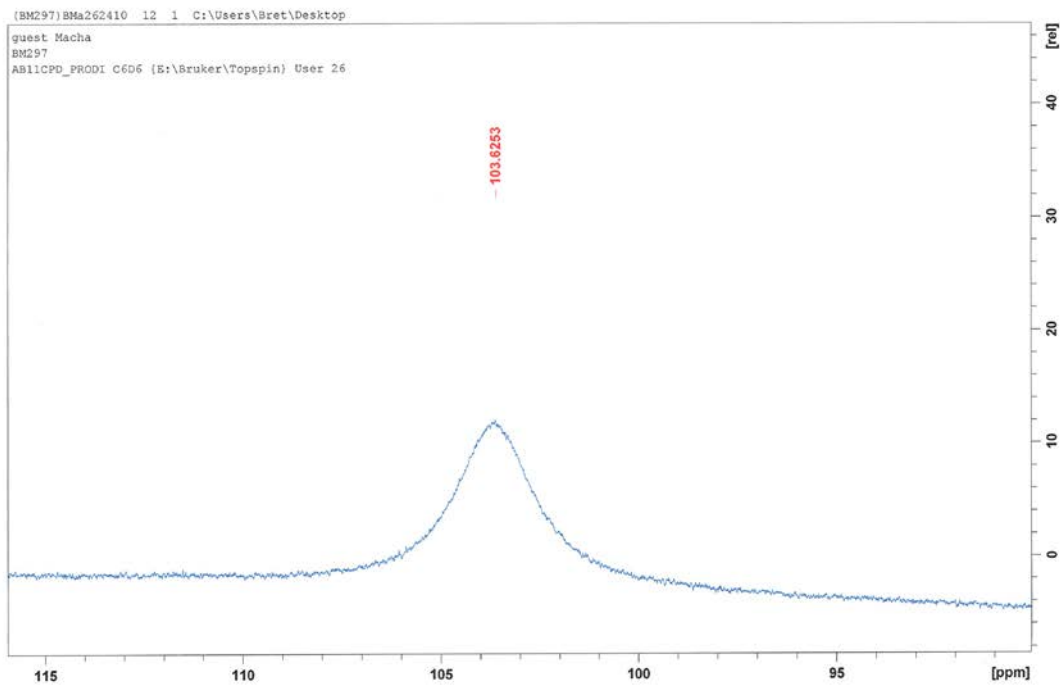


Fig. S21. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4** in C_6D_6 at RT.

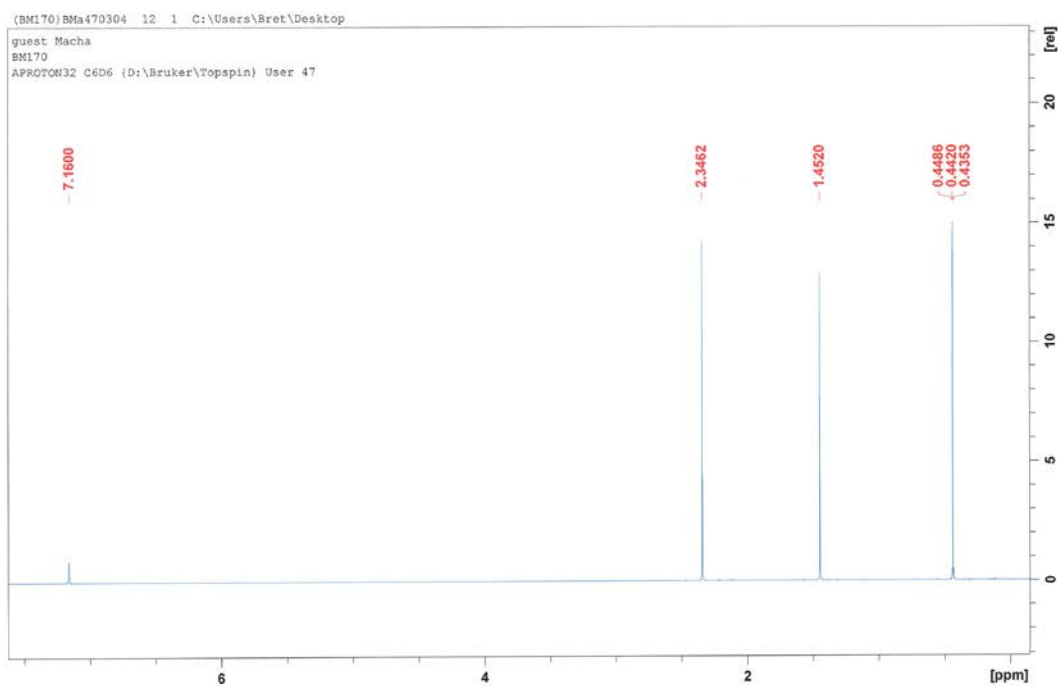


Fig. S22. ^1H NMR spectrum of **5** in C_6D_6 at RT.

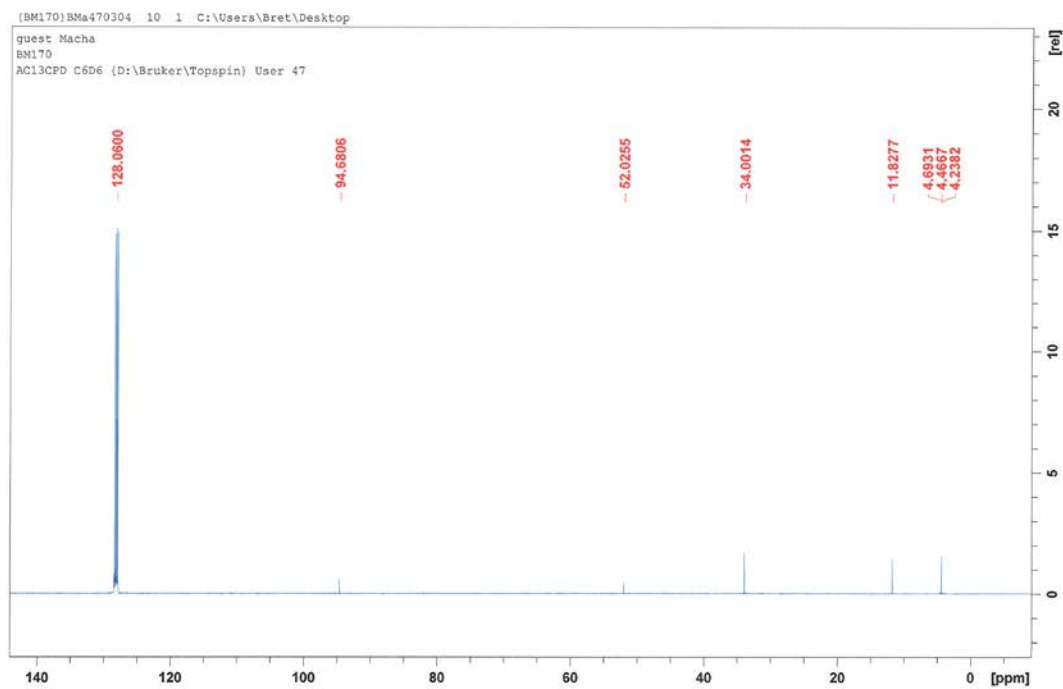


Fig. S23. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** in C_6D_6 at RT.

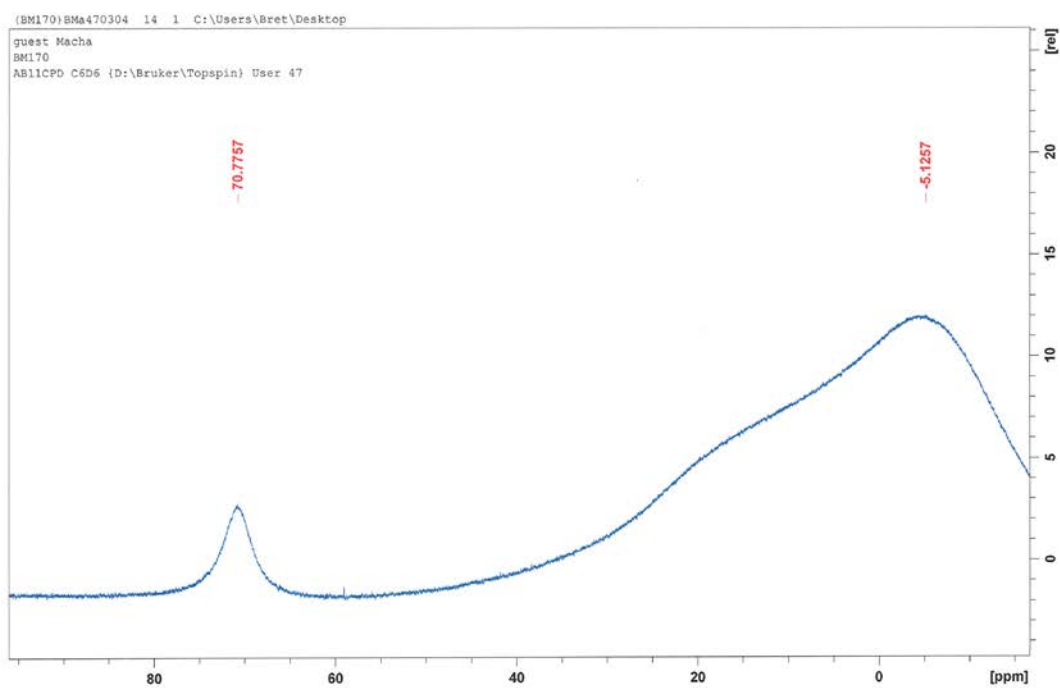


Fig. S24. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **5** in C_6D_6 at RT.

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